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Fracture Toughness and Impact Strength of Hollow Epoxy Particles-Toughened Polyester Composite

(Keliatan Rekahan dan Kekuatan Hentaman bagi Komposit Poliester Terisi Partikel Epoksi Berongga)

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ABSTRACT

Hollow epoxy particles (HEP) serving as reinforcing fillers were prepared using the water-based emulsion method in this study. HEP was incorporated into the polyester matrix at various loading, ranging from 0 wt% to 9 wt%, to toughen the brittle polyester thermoset. The polyester composites were prepared using the casting technique. The fracture toughness and impact strength of the polyester composites increased with increasing the HEP loading up to 5 wt%, after which there was a drop. The improvement in fracture toughness and impact strength is attributed to the good polymer-filler interaction. This finding was further supported by the scanning electron micrograph, in which it was shown that the polyester resin was interlocked into the pore regions of the HEP filler. The reduction in fracture toughness and impact strength of the polyester composite were believed to be attributed to the filler agglomeration. This filler-filler interaction would create stress concentration areas and eventually weakened the interfacial adhesion between the polymer matrix and the filler particles. Hence, lower fracture toughness and impact strength of the highly HEP-filled polyester composites (above 5 wt%) were detected.

Keywords: Filler loading; fracture toughness; hollow epoxy particles (HEP); impact strength; water-based emulsion

ABSTRAK

Partikel epoksi berongga (HEP) yang berperanan sebagai pengisi penguat telah disediakan dengan menggunakan teknik emulsi berasaskan air dalam kajian ini. Pengisi HEP ditambahkan ke dalam matriks poliester pada jumlah kandungan yang berlainan, iaitu daripada 0% berat sehingga 9% berat untuk meliatkan matriks poliester yang rapuh. Komposit poliester disediakan dengan menggunakan teknik tuangan. Keliatan rekahan dan kekuatan hentaman bagi komposit poliester bertambah dengan penambahan kandungan pengisi HEP sehingga 5% berat, tetapi dengan penambahan kandungan pengisi HEP yang berlebihan akan menyebabkan kemerosotan ke atas keliatan rekahan dan kekuatan hentaman komposit poliester. Peningkatan ke atas keliatan rekahan dan kekuatan hentaman adalah disebabkan oleh interaksi antara matriks polimer dan pengisi yang baik. Keputusan ini dapat disokong dengan mikrograf mikroskop elektron imbasan, dan ia telah menunjukkan bahawa resin poliester terikat ke dalam kawasan berongga pada pengisi HEP. Kemerosotan ke atas keliatan rekahan dan kekuatan hentaman bagi komposit poliester dipercayai disebabkan oleh penggumpalan pengisi. Penggumpalan antara pengisi-pengisi akan mewujudkan kawasan penumpuan tegasan dan akhirnya melemahkan pelekatan antara muka antara matriks polimer dan partikel pengisi. Oleh itu, keliatan rekahan dan kekuatan hentaman yang lebih rendah bagi komposit poliester terisi dengan jumlah kandungan pengisi HEP yang lebih tinggi (iaitu melebihi 5% berat) dapat diperhatikan.

Kata kunci: Emulsi berasaskan air; jumlah kandungan pengisi; keliatan rekahan; kekuatan hentaman; partikel epoksi berongga (HEP)

INTRODUCTION

Polyester resin has been utilized as the matrices for the composite materials and these advanced composite materials will eventually be used in a variety of industrial applications, such as in the aerospace, automobile and marine industries (Apicella et al. 1983; Kosar & Gomzi 2010; Visco et al. 2008). However, the brittleness of the polyester limits most of their applications that require toughness. Hence, plenty of efforts have been implemented to overcome the brittleness problem of the polyester matrix.

One of the methods is to incorporate the fillers into the thermoset matrix to enhance the impact resistance and fracture toughness of the composites. For example, rigid inorganic fillers such as calcium carbonate, clay, talc and kaolin are commonly introduced into the thermoset matrix to enhance the toughness of the composites. It are owing to the fact that these fillers are economic and are able to toughen the composites. Specifically, Astruc et al. (2009) introduced kaolin into the thermoset matrix to enhance the toughness of the composite. Johnsen et al. (2007) also found that the modulus and fracture toughness of the thermoset composite can be increased when a small amount of silica nano-particles is added into the thermoset matrix.

On the other hand, recent works by Watanabe et al. (2009) and Yuan et al. (2008) also found that the hollow spheres particles have been utilized as fillers to reinforce materials. Huang et al. (2009) and Zhao et al. (2008) stated that hollow microspheres are commonly used as low weight fillers for most materials since their low density and hollow structures are able to give rise to the 'micro-package' effect. Apart from that, Liang and Li (2007) also proved that the smooth spherical surfaces of hollow microspheres do not generate undesirable stress concentration area between the polymer-filler interface. Considering these advantages as mentioned, much efforts have been made to synthesize, develop and utilize the hollow microspheres in various filler applications. For example, hollow calcium carbonate particles is used in the paper filler application, whereas hollow mesoporous silica spheres is used in the membranes for the purpose of improvement in water absorption properties (Chen et al. 2010; Watanabe et al. 2009; Yuan et al. 2008).

Although plenty of research works have been done to investigate the applicability of various hollow spheres particles to toughen the thermoset matrix, to our best knowledge, there are still very limited research studies focused on hollow epoxy particles which are prepared using water-based emulsion technique in filler reinforcing applications. Hence, in this present study, the hollow epoxy fillers (HEP) were prepared. The effect of HEP filler loading on the fracture toughness and impact properties of polyester-based composites were investigated.

MATERIALS AND METHODS

MATERIALS

The epoxy resin 331 [diglycidyl ether of bisphenol A (DGEBA)] with the epoxide equivalent weight of 182-192 g/mol and polyamide hardener A026 used in this present study were supplied by Euro Chemo-Pharma Sdn. Bhd. Polyester resin (RP 9509GP) and methyl ethyl ketone peroxide (MEKP) catalyst with the density of 1.08 g/cm^3 were purchased from Zarm Scientific & Supplies Sdn Bhd (Malaysia). The calcium carbonate ($CaCO_3$) with the density of 2.71 g/cm^3 and hardness of 3 Mohs scale was provided by Malaysian Calcium Corporation Sdn. Bhd.

PREPARATION OF HOLLOW EPOXY PARTICLES (HEP)

The water-based emulsion was used to prepare hollow epoxy particle (HEP). At a predetermined ratio, the epoxy resin (DGEBA) and calcium carbonate ($CaCO_3$) were stirred together using mechanical stirrer at 300 rpm for 5 min. After that, the polyamide hardener was mixed into the epoxy mixture and stirred continuously for 2 min until a homogeneous mixture was obtained. The epoxy mixture was then poured into the water medium and the emulsion process was conducted using homogenizer at the speed of 15,000 rpm for 9 min. Finally, the mixture was placed in an oven at 80°C for 24 h for further curing process. The fine powder of HEP filler (approximately 1.95 – 41.53 μm) could be produced after the cured epoxy sample was grinded.

PREPARATION OF HEP-FILLED POLYESTER COMPOSITES

Polyester composites were prepared using casting method. Firstly, the HEP powders were incorporated into the polyester resin at different loading, ranging from 0 wt% to 9 wt%. The epoxy mixtures were stirred homogeneously before the MEKP catalyst was added. After that, the epoxy mixtures were poured into rubber mold and subjected to thermal curing in an oven at 80°C for 3 h.

MECHANICAL CHARACTERIZATION OF HEP-FILLED COMPOSITES

To investigate the effect of HEP filler loading on the mechanical properties of polyester based composite, fracture toughness test were conducted according to ISO 13586: 2000 standard method using Instron machine model 3366. The dimension of the specimen was about 60 mm × 12 mm × 3 mm with the crack length-to-width ratio (a/W ratio) of 0.5. The initial crack was introduced on the specimen using razor blade before the fracture toughness test. The fracture toughness test was conducted at a crosshead speed of 10 mm/min. The fracture toughness values, K_{IC} of the polyester composites with different HEP loading were determined using the following equations:

$$y = 1.93 - 3.07\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.11\left(\frac{a}{W}\right)^3 + 25.8\left(\frac{a}{W}\right)^4, \quad (1)$$

$$K_K = \frac{3PSa^{1/2}y}{2tw^2}, \quad (2)$$

where y is a geometrical correction factor, a is the notch length (mm), W is the specimens width (mm), S is the span length (mm), P is the load at peak (N) and t is the specimen thickness (mm).

The fractured surfaces of the HEP-reinforced epoxy composites after fracture toughness testing were observed using a field-emission scanning electron microscope (FESEM) model Zeiss Supra 35VP (USA). The sample was coated with platinum/gold prior to FESEM characterization.

The impact test was conducted using impact test machine (Zwick impact tester) according to the ASTM D 6110. The charpy method was carried out using notched samples with the dimensions of 60 mm × 12 mm × 3 mm and notch length of 2 mm. The impact strength of composites specimens were calculated in unit kJ/m^2 according to:

$$\text{Impact strength} = \frac{W}{b_n \times h}, \quad (3)$$

where W is the impact energy absorbed (J), b_n is the width of sample minus notch length (mm) and h is the thickness of sample (mm).

RESULTS AND DISCUSSION

Figure 1 exhibits the effect of the HEP filler loading on the fracture toughness of the polyester composite. It was found that the fracture toughness of the composite increased with the increase of HEP filler loading up to 5 wt%. The continuous increment in fracture toughness of composite is believed to be due to the capability of the filler particle to resist the crack propagation before fracture taken place. The HEP filler particles will act as an obstacle to the applied force through the crack-pinning mechanism. It can increase the crack path length as the cracks are forced to be propagated by bowing around the filler particle. Hence, the increment in the line energy will lead to the enhancement of the fracture toughness of the polyester composites. This is particularly in line with the finding reported by Fu et al. (2008) and Wetzel et al. (2006) who mentioned that the toughness of the polymer system can be improved since the crack pinning mechanism give rise to an increase in the line energy. In addition, the highest fracture toughness of the 5 wt% HEP-filled composite is due to the good interaction between HEP filler and polymer matrix. This is attributed to the fact that the interlocking of the polyester resin into the pores region of the HEP filler, as shown in Figure 2(b), can raise the capability of the composite to absorb more energy before fracture initiates. As a result this "interlocking" effect will increase the resistance of the HEP-filled composites against the crack deformation. Therefore, the improvement in the fracture toughness of polyester composite at the optimum HEP loading as shown in Figure 1 can be justified.

However, the fracture toughness of the composite decreases as the filler loading exceeds 5 wt%. This might be due to the agglomeration of the filler particles as illustrated in Figure 2(c). The poor dispersion of the HEP filler particles throughout the polymer matrix and the formation of larger cluster of filler agglomeration will act as stress concentration areas. This will result in the reduction of the resistivity of the composite against the crack propagation and subsequently deteriorate the fracture toughness of the composite (Low & Abu Bakar 2012). Hence, a decrease in fracture toughness of the polyester composites filled with relatively high HEP filler loading is detected.

Figure 2 displays the fractured surface of the neat polyester, 5 wt% HEP-filled polyester composite and 9 wt% HEP-filled polyester composites after the fracture toughness test. The fracture behavior of each composite can be explained based on their fractured morphologies. Accordingly, a relatively smooth fracture surface of the neat polyester Figure 2(a) indicates the catastrophic brittle fracture of the thermoset. This implied the lower resistance of the neat polyester against the crack propagation and deformation. In contrast to the neat polyester, a more tortuous and rougher surface is observed in Figure 2(b) on the fractured surface of the 5 wt% HEP-filled polyester composite. A number of cavitated holes as a results of the HEP fillers being 'pulled' out from the polyester matrix with the external forces applied, are dispersed throughout the fractured surface of the composite. This incident showed the increase in resistance against the

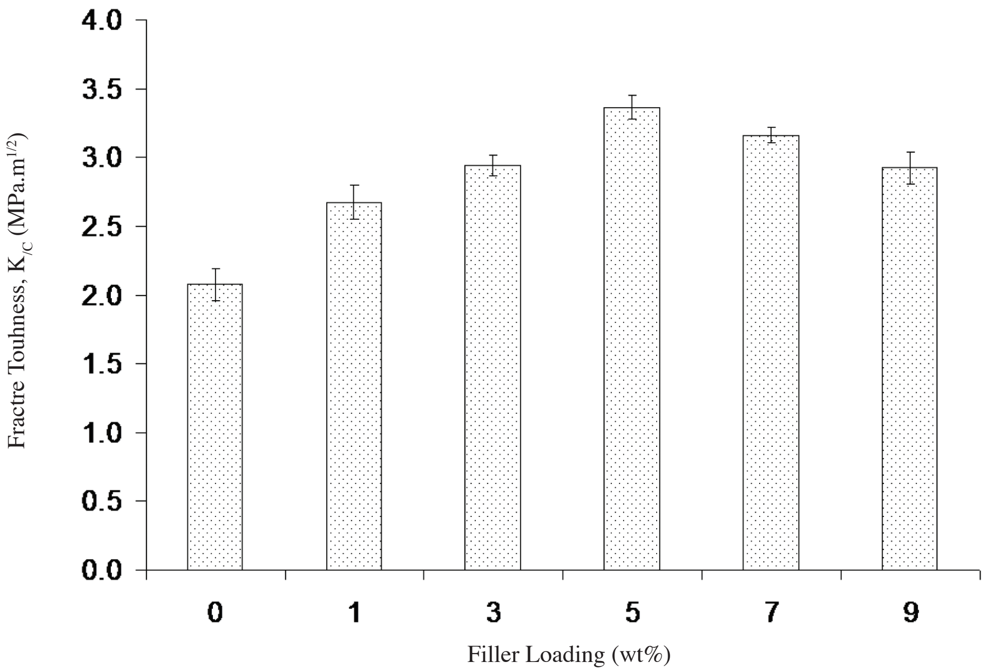

FIGURE 1. Fracture toughness of the polyester composite reinforced with different HEP filler loading

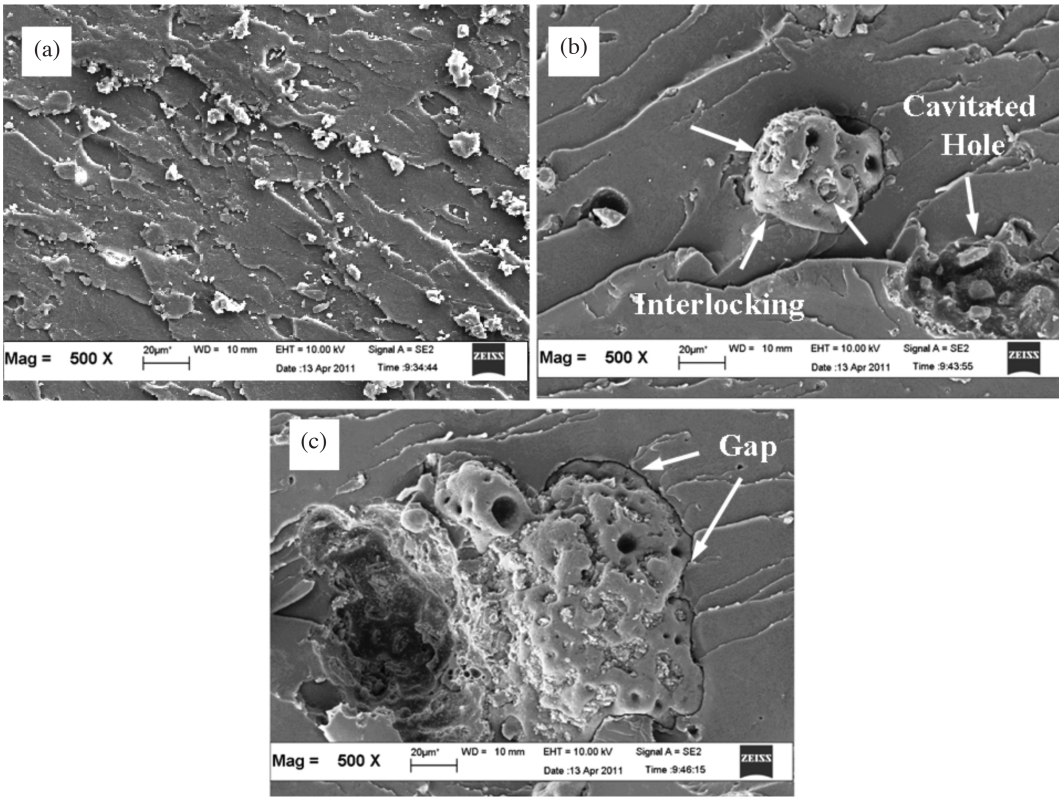

FIGURE 2. SEM micrographs of the fracture surface of (a) neat polyester, (b) 5 wt% HEP-filled polyester composite and (c) 9 wt% HEP-filled polyester composite

deformation and hence reduced the crack propagation rate throughout the polyester matrix (Low & Abu Bakar 2011). Therefore, this gives rise to a higher fracture toughness. However, at higher HEP filler loading which exceeding the optimum loading, agglomeration of fillers and the presence of small gap between the polyester matrix and HEP filler are observed in Figure 2(c). Poor polymer-filler interaction and the creation of stress concentration area due to agglomeration will reduce the fracture resistance of the composite. Thus, a decrease in fracture toughness properties of the polyester composite is observed as the filler loading exceeds 5 wt%.

Figure 3 shows the impact strength of the polyester composite filled with different HEP filler loading, ranging from 0 wt% to 9 wt%. It is noticed that the polyester composite possesses the highest impact strength if it is filled with 5 wt% HEP loading. The improvement in impact strength with HEP loading up to its optimum filler loading is attributed to the aforementioned good polymer-filler interaction. The interlocking of the polymer matrix into the pore regions of the HEP fillers as shown in Figure 2 gives rise to a good interaction between the polymer and the filler. This will help resist and eventually stop the crack propagation throughout the polymer matrix when the composite is subjected to an impact load. The increment in the crack length path is also due to the filler particles which will increase the ability of the composites to absorb greater energy before failure. Gupta et al. (2001) also reported in their research study that the presence of fillers will resist crack propagation and prolong the crack length path.

However, a reduction in the impact strength is observed when the HEP filler loading added is greater than the optimum loading. This is mainly due to the filler-filler interaction that will caused agglomeration, which leads to a poor interaction between the HEP filler and the polymer matrix (Suresha et al. 2010; Zaini et al. 1996). These undesirable polymer-filler interaction and the existence of weak interface region in the polymer matrix may attribute to the reduction in the resistance against the crack propagation of the system. Shivamurthy et al. (2009) also agreed that filler-filler aggregation will act as a stress concentrator to alter the impact properties of the composite. Therefore, the ability of the composite to absorb external applied force reduces due to the presence of stress concentrators. So, lower impact strength is obtained for those composite filled with high HEP loading.

CONCLUSION

Hollow epoxy particle (HEP) were produced using water-based emulsion technique. The fracture toughness and impact strength of the polyester composites increase with increasing the HEP filler loading up to 5 wt%. The enhancement in toughening on the polyester composite is mainly attributed to the good polymer-filler interaction since the polyester resin interlocks into the pores regions

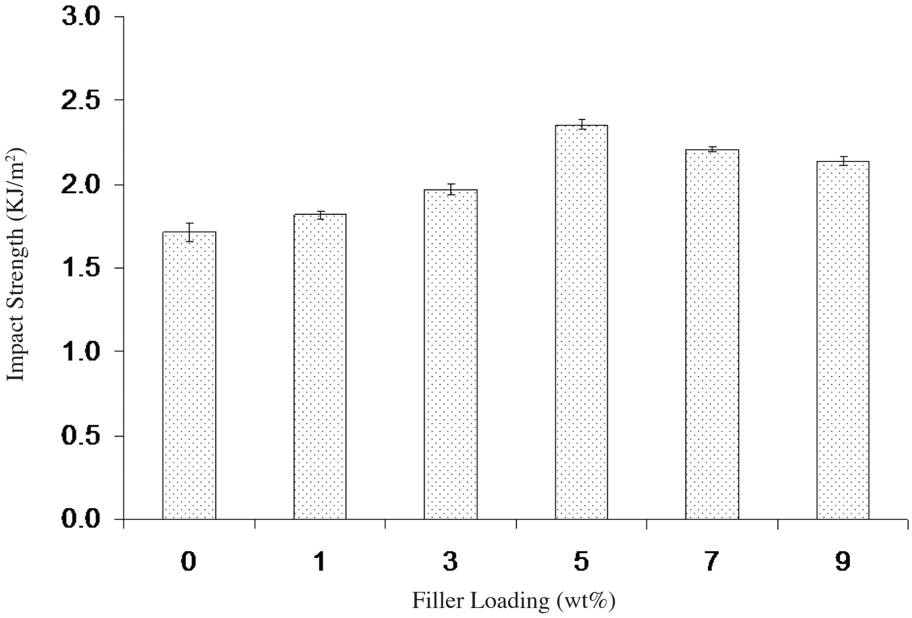

FIGURE 3. Impact strength of the polyester composite reinforced with different HEP filler loading

of the HEP fillers. The fracture toughness and impact properties of the polyester composite are deteriorated once the HEP filler loading incorporated into the polyester matrix exceeding the optimum HEP filler loading. Filler-filler interaction which leads to agglomeration is one of the factors giving rise to the reduction of the fracture toughness and impact properties of the HEP-filled polyester composite.

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